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A simple scaling derivation of the shear thinning power-law exponent in entangled polymer melts

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ABSTRACT

By suggesting that the polymer dynamics in entangled polymer melts possesses the property of dynamical self-similarity, we argue that the power-law exponent of the Carreau-Yasuda law, which empirically describes the shear thinning effect of the polymer melt viscosity, is inversely proportional to the exponent of the molecular mass dependence of the terminal relaxation time. This finding is obtained in cases where the shear rate dependence of the segmental relaxation time is negligible. If such dependence is essential, the Carreau-Yasuda law is slightly modified at high shear rates: instead of a power-law dependence with a small shear rate independent exponent, a weaker logarithmic dependence is found both for shear rate and molecular mass dependence, which resembles the approach to zero of an effective shear rate and molecular mass dependent power-law exponents at sufficiently high shear rates.

For several decades it is well known from experimental observations, that in entangled polymer melts the steady state viscosity is dependent from shear rate in accordance with the so-called Carreau-Yasuda law (see, for example [1–3] and literature cited therein):

$$\eta(\dot{\gamma}) = \eta_0\left[1+(\lambda\dot{\gamma})^a\right]^{\frac{n-1}{a}} \tag{1}$$

where η_0 is the zero shear viscosity of the polymer melt, $\dot{\gamma}$ is the shear rate, λ is a characteristic time on the order of the polymer chain terminal relaxation time $\lambda \propto \tau_1$, n is the power-law exponent and a is the transition width parameter between Newtonian and the non-Newtonian regime. This phenomenon of decreasing measured viscosity with increasing shear rate is widely known as "shear thinning" and is a central aspect in the rheology of polymer systems.

For entangled polymer melts, experimental values of the exponent parameters obtained from fitting the shear-rate dependent viscosity typically lie in the interval: $n = 0.2 \div 0.4$ and $a \approx 1 - n$, see [1–3]. For large Weissenberg numbers $Wi \equiv \tau_1\dot{\gamma} > 1$, this region being the main object of this communication, expression (1) can be approximated as

$$\eta(\dot{\gamma}) \cong \eta_0(\lambda\dot{\gamma})^{n-1} \propto \eta_0(\tau_1\dot{\gamma})^{n-1} \tag{2}$$

The classical Doi-Edwards [4] tube model can qualitatively describe the shear thinning phenomenon, but predicts a power-law dependence with an exponent $n = -0.5$, indeed much different than those found experimentally. Additional phenomenological modifications of the tube models, making it more isotropic, essentially improve the predictions within the experimentally investigated region (see, for instance [5], and literature therein), but nevertheless does not yet present a simple qualitative picture of the essence of shear thinning in entangled polymer melts. In this paper we present a rather general and simple argumentation showing that the discussed power-law exponent can be directly related to the scaling power-law exponent α of the molecular mass dependence of the polymer melt terminal relaxation time:

$$\tau_1 \propto \begin{cases} \tau_s N_e^2 \left(\dfrac{N}{N_e}\right)^{\alpha} & \text{if } N > N_e \\ \tau_s N^2 & \text{if } N < N_e \end{cases} \tag{3}$$

where $N_e = N_c/2$ is the number of Kuhn segments between two neighboring entanglements, N_c is the critical molecular mass expressed in number of Kuhn segments, and τ_s is the segmental relaxation time, while the experimentally observed exponent is $\alpha = 3.2 \div 3.7$.

The qualitative idea behind this derivation is very simple. In equilibrium, a polymer chain has a conformation close to a three-

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